

Selective Solvent-Free and Additive-Free Oxidation of Primary Benzylic C–H Bonds with O_2 Catalyzed by the Combination of Metalloporphyrin with N-Hydroxyphthalimide

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Abstract

A protocol for solvent-free and additive-free oxidation of primary benzylic C–H bonds with O_2 was presented through adjusting the combination of metalloporphyrins and NHPI as binary catalysts to overcome the deficiencies encountered in current oxidation systems. The effects of reaction temperature, porphyrin structure, central metal, catalyst loading and O_2 pressure were investigated systematically. For the optimized combination of T(2-OCH₃)PPCo and NHPI, all the primary benzylic C–H bonds could be functionalized efficiently and selectively at 120 °C and 1.0 MPa O_2 with aromatic acids as the primary products. The selectivity towards aromatic acids could reach up to 70–95% in the conversion of more than 30% for most of the substrates possessing primary benzylic C–H bonds in the metalloporphyrin loading of 0.012% (mol/mol). And the superior performance of T(2-OCH₃)PPCo among the metalloporphyrins investigated was mainly attributed to its high efficiency in charge transfer and fewer positive charges around central metal Co (II) which favored the adduction of O_2 to cobalt (II) forming the high-valence metal-oxo complex followed by the production of phthalimide N-oxyl radical (PINO) and the initiation of the catalytic oxidation cycle. This work would provide not only an efficient protocol in utilization of hydrocarbons containing primary benzylic C–H bonds, but also a significant reference in the construction of more efficient C–H bonds oxidation systems.

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Graphic Abstract

The solvent-free and additive-free oxidation of primary benzylic C–H bonds with O_2 was presented through adjusting the combination of metalloporphyrins and NHPI as binary catalysts, and the highest selectivity towards aromatic acid reached up to 95.1% with the conversion of 88.5% in the optimized combination of T(2-OCH₃)PPCo and NHPI.



Keywords Benzylic C-H bond · Oxidation · Molecular oxygen · Metalloporphyrin · Selectivity

1 Introduction

The direct, convenient, and selective functionalization of C-H bonds in hydrocarbons through oxidation reactions has always been an extremely useful, challenging, and fascinating research topic, not only in the industrial chemistry but also in the academic research on chemistry [1-5]. In these significant transformations, the widely available and inexpensive hydrocarbons are converted to high value-added hydroperoxides, alcohols, aldehydes, ketones, acids and esters, and all of these oxygen-containing compounds are essential fine chemicals and chemical intermediates [1, 6-8]. Among these processes, one typical example is the oxidation of primary benzylic C-H bonds, in which methylbenzene and its derivatives are converted to valuable benzyl hydroperoxide, benzyl alcohol, benzaldehyde, benzoic acid, and their derivatives [9–12]. These oxidation products of primary benzylic C-H bonds have been applied widely as food additives, flavors, fragrances, medicines, and the irreplaceable intermediates in the manufacture of pharmaceuticals, perfumes, agricultural chemicals, dyes, resins, and synthetic polymer fibers, possessing huge market demand [7, 13-18]. To realize the transformation from primary benzylic C-H bonds to these oxygen-containing products, a series of oxidants can be employed, such as iodosylbenzene [19, 20], potassium persulfate [1, 21], tert-butyl hydroperoxide [11, 22, 23], hydrogen peroxide [24–26], molecular oxygen [3, 27, 28] and so on [29, 30], but molecular oxygen (O_2) has been regarded as the first choice for its readily availability, high atom economy, cleanness and environmental-friendliness. Thus in the current industrial processes, the oxidation of primary benzylic C-H bonds is usually carried out with O₂ as oxidant in the presence of homogeneous cobalt (II) acetate or manganese (II) acetate as catalyst and bromide as promoter in the solvent of acetic acid [18, 31-34]. For the high inertness of primary benzylic C-H bonds and triplet oxygen molecule, high reaction temperature above 160 °C and high oxygen pressure must be employed [18, 32–34]. The existence of solvent acetic acid and promoter bromide, not only would bring about some difficulties to the separation of oxidation products and catalysts, and increase the waste discharged into the environment, but also would lead to serious corrosion to the production equipment, which make the current industrial processes not so compatible with the requirements of green chemistry. In addition, due to the high reaction temperature, the over-oxidation of obtained oxygen-containing products to CO₂ might occur, hence the conversion of methylbenzene in current process was controlled below 15% with less efficiency [18, 31-34]. Therefore, considering the huge market demand and high value of the products, and the deficiencies encountered in current oxidation process, it is a great urgency to develop a mild route to realize the selective and efficient oxidation of primary benzylic C–H with O_2 under solvent-free conditions in the absence of any additive. To achieve this purpose, suitable and convenient catalytic system is the key.

The catalytic systems combined by N-hydroxyphthalimide (NHPI) or its analogues with transition metal ions such as cobalt (II) and manganese (II) have been applied widely in the oxidation of C-H bonds in various hydrocarbons with $O_2[14, 18, 32, 35-40]$. High efficiency and mild conditions usually could be obtained. Arzumanyan and coworkers reported the selective oxidation of primary benzylic C-H bonds in 4-tolylsiloxanes with O₂ catalyzed by the combination of N-hydroxysuccinimide (NHSI) and cobalt (II) acetate at 40-60 °C under atmospheric pressure in acetonitrile, and the yield of 4-carboxyphenylsiloxanes reached up to 96%, in which the primary benzylic C-H bonds were converted to carboxylic acids efficiently and smoothly [40]. Shi and co-workers documented the efficient oxidation of methylbenzene by O_2 catalyzed by the combination of N-hydroxyphthalimide (NHPI) and CoOx immobilized on SiO₂ at room temperature under atmospheric pressure in hexafluoropropan-2-ol, and the conversion reached up to 91.2% with the selectivity of 68.8% towards benzaldehyde and 20.3% towards benzoic acid, in which the utilization of hexafluoropropan-2-ol as solvent was the key for the outstanding conversion and selectivity [14]. Zhang et al. reported the selective oxidation of primary benzylic C-H bonds with O₂ catalyzed by the combination of NHPI and Co(OAc)₂ at 100 °C under atmospheric pressure employing imidazolium-based ionic liquid as additives, and for methylbenzene as substrate, the conversion reached up to 80% with the selectivity of 97.5% towards benzoic acid [41]. Besides these, the combination of NHPI with copper nanoparticles on N-doped graphene in acetone [39], NHPI with cobalt (II) acetate in hexafluoropropan-2-ol [38], NHPI and its analogues with cobalt (II) acetate in acetonitrile [42], immobilized NHPI with cobalt (II) in acetic acid [34], immobilized N, N-dihydroxypyromellitimide (NDHPI) with cobalt (II) in acetonitrile [32, 33], were also applied in the oxidation of benzylic C-H bonds using O2 as oxidant under mild conditions. Acceptable conversion and selectivity usually could be achieved.

Metalloporphyrins are a family of useful and important transition metal complexes, and have been employed extensively in the oxidative functionalization of C–H bonds in hydrocarbons as catalysts [5, 43–47]. Owing to the high efficiency of metalloporphyrins in the activation of O_2 , the catalyst loading in one ten-thousandth of substrates would be adequate to achieve the oxidative functionalization of C–H bonds, thus the combination of NHPI with metalloporphyrins could make the oxidation of C–H bonds in hydrocarbons consume less transition metal catalysts and approach the requirement of green chemistry [48, 49]. For instance, Guo and co-workers

documented the oxidation of methylbenzene using O_2 catalyzed by the combination of NHPI and porphyrin manganese (III) in acetic acid with methanol as additive or in the presence of cetyl trimethyl ammonium bromide (CTAB) as additive, and the conversion reached up to 41.0% with the selectivity of 70.6% towards benzoic acid and 25.0% towards benzaldehyde [50–52]. Zhu et al. reported the oxidation of methylbenzene using O_2 catalyzed by the combination of NHPI with immobilized phthalocyanine iron (II) in acetonitrile, and the conversion was 35.3% with the selectivity of 71.8% to benzoic acid and 20.1% to benzaldehyde [53]. Despite the satisfying conversion and selectivity under mild conditions, the presence of solvent and additive became the main obstacle in the extensive industrial application of current route employing the combination of NHPI and transition metal complexes as catalysts.

Therefore, in the endeavor to achieve the efficient oxidative functionalization of C-H bonds in hydrocarbons to valuable oxygen-containing products in our group, we have been focusing on the solvent-free and additive-free route under mild conditions involving metalloporphyrins all the time [54–58]. And in this work, we carried out the selective solvent-free and additive-free oxidation of primary benzylic C-H bonds using O₂ as oxidant. Based on the systematical screen on the structure and performance of metalloporphyrins, primary benzylic C-H bonds were transformed to their oxygen-containing products efficiently without any solvent and additive under mild conditions employing the combination of NHPI with porphyrin cobalt (II) as catalyst. For the representative compounds of primary benzylic C-H bonds, the conversion of methylbenzene and 4-methyl nitrobenzene reached up to 35.1% and 49.4% with aromatic carboxylic acids as major products (selectivity of 92.3% and 64.5% respectively) at 120 °C and 1.0 MPa O₂ pressure. The major superiorities of this protocol are no solvent, no additive, mild conditions, higher conversion and selectivity compared with the current oxidation systems, which make the route for primary benzylic C-H bonds oxidation reported here possess not only huge potential in industrial application, but also enormous reference value for other C-H bonds oxidative functionalization. To our best knowledge, this work is also a very convenient, practical and novel example in the efficient utilization of widely available and inexpensive hydrocarbons, and would act as a significant reference in both academic research and industrial application for more efficient utilization of hydrocarbons.

2 Experimental Section

2.1 Materials

Benzaldehyde and its derivatives used as reactants in the porphyrin syntheses were mainly purchased from Shanghai Macklin Biochemical Co. Ltd., Adamas Reagent Co. Ltd., Xilong Chemical Reagent Co. Ltd., and Shanghai Energy Chemical Co. Ltd., China. Pyrrole in the syntheses of porphyrins was purchased from Xilong Chemical Reagent Co. Ltd., and was purified before used through reduced pressure distillation. The metal acetates such as cobalt (II) acetate, manganese (II) acetate, copper (II) acetate, iron (II) acetate in the metalloporphyrins syntheses were purchased from Adamas Reagent Co. Ltd. and Shanghai Energy Chemical Co. Ltd. China. Methylbenzene, substituted methylbenzene and their oxidation products in oxidation of primary benzylic C-H bonds were purchased from Shanghai Macklin Biochemical Co. Ltd., Adamas Reagent Co. Ltd., Xilong Chemical Reagent Co. Ltd., and Shanghai Energy Chemical Co. Ltd., China. All the chemicals used in this work were analytical reagents and were not purified any more before used unless otherwise noted.

2.2 Characterizations

The qualitative characterizations of porphyrins and metalloporphyrins such as ¹H NMR, ¹³C NMR, and ESI-MS were carried out on the Bruker AVANCE III 500 MHz NMR spectrometer, and Agilent 6210 LC/TOF mass spectrometer respectively. In the NMR analyses, tetramethylsilane was used as internal standard, and $CDCl_3$ and $DMSO-d_6$ as solvents. In the ESI-MS analyses, direct injection mode was adopted with CH₂Cl₂ as solvent. The UV-Vis analyses were performed on a HITACHI U-3900 spectrometer in a quartz cuvette at room temperature, and the sample was dissolved in DMF. The thermal gravimetric analyses (TGA) were carried out on a PerkinElmer Diamond TG/ DTA instrument to study the thermal stability of metalloporphyrins, and all the TG analyses were conducted in the temperature range of room temperature to 800 °C (10 °C/min) under the atmosphere of air. The redox activity analyses of metalloporphyrins used as catalysts were conducted on the ZAHNER Zennium electrochemical workstation at 25 °C under the atmosphere of nitrogen. In the electrochemical measurements, three-electrode system was adopted containing working electrode (a glassy carbon), counter electrode (a platinum wire), and reference electrode (Ag/AgCl), and tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte (0.025 mol/L in DMF).

2.3 Syntheses of Metalloporphyrins

The metalloporphyrins were mainly synthesized through the condensation of benzaldehyde or its derivatives with pyrrole, and then metallization of the obtained porphyrins according to the procedure reported [59–66]. In the typical procedure of porphyrin syntheses, benzaldehyde or its derivatives (150 mmol) was heated to refluxing (145 °C) with stirring

in propionic acid (450 mL) under the nitrogen protection, followed by the addition of redistilled pyrrole (150 mmol) dropwise under refluxing conditions. After refluxing for 2.0 h in the shield from ambient light, the resultant mixture was cooled in air to room temperature and kept standing until a large amount of solid appeared. Then the solid was collected through suction filtration and suspended in methanol (200 mL) with stirring for 6.0 h. The collected purplish red precipitate was washed successively using methanol (2×100 mL) and purified through silica column chromatography separation with cyclohexane and dichloromethane as eluent (10:1-4:1, volume/volume).

After dried under reduced pressure for 8.0 h at 80 °C, the obtained porphyrin (0.20 mmol) was dissolved in DMF (60 mL) with corresponding anhydrous metal acetate (2.0 mmol), and the obtained solution was heated to refluxing (150 °C) with stirring under N₂ atmosphere. The refluxing solution was kept stirring for 24.0 h, and cooled to room temperature in air. Then DMF was removed under reduced pressure through rotary evaporation, and the resultant solid was dissolved in dichloromethane (60 mL) to form a purplish red solution, which was washed with water five times $(5 \times 200 \text{ mL})$ until the upper water layer became clear and colorless, and dried over anhydrous Na2SO4. Following rotary evaporation, obtained purple solid was further purified through silica column chromatography separation with cyclohexane and dichloromethane as eluent (4:1-1:1, volume/volume). All of the metalloporphyrins synthesized herein were dried under reduced pressure for 8.0 h at 80 °C before used. More details for the syntheses of metalloporphyrins have been demonstrated in the Electronic Supplementary Material.

2.4 Oxidation of Primary Benzylic C-H Bonds

All the oxidation of primary benzylic C-H bonds were conducted in a 100 mL stainless steel autoclave reactor. In order to eliminate the uncertain effect of the presence of metal element, a Teflon liner was employed in all the oxidation reaction. In a typical procedure, methylbenzene or substituted methylbenzene (50 mmol) were sealed in the autoclave reactor in the presence or absence of catalysts, and heated to the set reaction temperature with stirring. After the temperature reached, O₂ was injected into the reactor to obtain the set pressure, and the reaction mixture was kept heating and stirring for 8.0 h. Then the reactor was cooled by cold water to room temperature. When the autoclave reactor was opened, acetone (50 mL) was added to dilute the reaction mixture followed by the addition of triphenylphosphine (10 mmol) to reduce the unconverted hydroperoxide to alcohol. After stirring for another 30 min at room temperature, the obtained reaction mixture was totally transferred into a volumetric flask (100 mL) employing acetone as solvent. In succession,

quantitative analyses were carried out employing GC and HPLC to determine the conversion and selectivity in the primary benzylic C–H bonds oxidation.

2.5 Product Analyses

The unreacted substrates possessing primary benzylic C-H bonds, and oxidation products were confirmed qualitatively through comparison with the authentic samples, especially the retention times in GC and HPLC analyses. The quantitative analyses of the major products, aromatic carboxylic acids, were conducted on a high performance liquid chromatograph (HPLC) (Thermo Scientific Ultimate 3000) with 2-naphthalenecarboxylic acid as the internal standard. And the model of chromatographic column was Amethyst C18-H (250 mm \times 4.6 mm \times 0.25 µm), and the detector was Ultimate 3000 Photodiode Array Detector. The quantitative analyses of other oxidation products, such as alcohols, aldehydes and peroxides were carried out on a gas chromatograph (Thermo Scientific Trace 1300) with naphthalene as the internal standard. The model of chromatographic column was TG-5MS capillary column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$), and the detector was Flame Ionization Detector. The quantity of peroxide was mainly obtained based on the triphenvlphosphine oxide which was produced through reduction of hydroperoxide by triphenylphosphine quantitatively.

3 Results and Discussion

3.1 Characterizations

In addition to the NMR and ESI–MS spectra, the porphyrins and metalloporphyrins were characterized qualitatively through the UV-Vis absorbance analyses. It was demonstrated in Figs. 1 and S1 that, for all the porphyrins and metalloporphyrins measured, the characteristic absorbance peaks in about 425 nm were found, which were mainly attributed to the Soret band absorbance of porphyrins and metalloporphyrins, and indicated the correctness in molecular structure [51, 67–71]. And for the difference in molecular structure and solubility, both of porphyrins and metalloporphyrins exhibited diverse intensity in UV-Vis absorbance spectra. Figures 2 and S2 were the TGA plots of representative metalloporphyrins in the atmosphere of air, in which it could be found that all of the metalloporphyrins measured possessed well thermal stability before 300 °C, even in the oxidative atmosphere. Thus, to some extent, it is feasible to employ metalloporphyrins as catalysts in oxidation of primary benzylic C-H bonds at the temperature not too high (below 150 °C). Then the cyclic voltammograms of metalloporphyrins were measured in a DMF solution of tetrabutylammonium hexafluorophosphate (0.025 mol/L) to check their redox behaviors employed as catalysts in oxidation of primary benzylic C-H bonds. As illustrated in Fig. 3, obvious redox currents were detected under a suitable external voltage. The good performance in electron transfer indicated that the metalloporphyrins utilized in this work possessed the possibility to perform as catalysts in oxidation of primary benzylic C-H bonds.

3.2 Oxidation of Primary Benzylic C–H Bonds Catalyzed by Metalloporphyrin and N-Hydroxyphthalimide

With the objective to realize the selective, solvent-free and additive-free oxidation of primary benzylic C–H bonds, the combination of metalloporphyrin and NHPI was employed



Fig. 1 UV–Vis spectra of porphyrins (a) and metalloporphyrins (b) in DMF $(2.0 \times 10^{-6} \text{ mol/L or saturated})$



Fig. 2 The TGA plots of representative metalloporphyrins



Fig. 3 Typical cyclic voltammograms of metalloporphyrins in DMF in scan rate of 100 mV/s

as binary catalysts in this work. For the mild conditions, we tried to carry out the catalytic transformation at lower temperature to avoid the unselective autoxidation, and 4-methyl nitrobenzene was employed as the representative substrate to screen a suitable reaction temperature. As demonstrated in Tables 1 and S1–S4, there was not any oxidation transformation of 4-methyl nitrobenzene observed before 140 °C, no matter in the presence of metalloporphyrins as catalysts or not. So it might not be a sensible choice to conduct the oxidation of primary benzylic C–H bonds only using metalloporphyrins as catalysts. When N-hydroxyphthalimide (NHPI) in molar ratio of 5% was employed as catalyst, the catalytic oxidation of 4-methyl nitrobenzene could be obtained in the

whole temperature range from 70 to 120 °C (Table S5). And the conversion reached up to 16.6% with the selectivity of 61.1% towards 4-nitrobenzoic acid. Considering the mild conditions, the reaction temperature was kept not higher than 120 °C. Although the catalytic transformation of primary benzylic C-H bonds was gained employing NHPI as catalyst, the conversion of 4-methyl nitrobenzene (16.6%) was not so competitive and satisfying. Thus metalloporphyrins were introduced to form binary catalysis system. For the representative metalloporphyrin T(4-Cl)PPCo, only 0.012% in molar ratio was employed to form binary catalysis system with NHPI, the conversion of 4-methyl nitrobenzene being increased dramatically from 16.6 to 31.3% with selectivity above 60% towards 4-nitrobenzene acid. And when the molar ratio of NHPI was increased to 10% (mol/mol), the conversion increased further to 40.4% with the selectivity above 50% towards aromatic acid. The tremendous promotion in catalytic activity was mainly attributed to the delicate cooperation between metalloporphyrin and NHPI, in which the metalloporphyrin acted as initiator, and the hydrogen atom in the hydroxyl of NHPI molecule was abstracted by the high-valence metal-oxo complex obtained from the interaction of metalloporphyrin and O₂ firstly, then the formed phthalimide N-oxyl radical (PINO) initiated the catalytic oxidation cycle of primary benzylic C-H bonds [72, 73]. Compared with the employment of metalloporphyrin or NHPI as unitary catalyst, the combination of metalloporphyrins and NHPI is a more efficient catalytic system for the selective, solvent-free and additive-free oxidation of primary benzylic C-H bonds, based on which the catalytic transformation was obtained under very mild conditions (120 °C) with aromatic acids as primary products (selectivity above 50%).

3.3 Effect of Porphyrin Structures on Oxidation of Primary Benzylic C–H Bonds

The performance of metalloporphyrins in catalytic oxidation was influenced dramatically by the structure of ligands, which resulted in the excellent adjustability in the catalytic properties. To obtain the efficient oxidation of primary benzylic C–H bonds under mild conditions, the effect of the porphyrin ligands on the oxidation of primary benzylic C–H bonds catalyzed by the combination of metalloporphyrins and NHPI was investigated systematically employing 4-methyl nitrobenzene as representative substrate at 120 °C and 10% NHPI (mol/mol). As illustrated in Tables 2 and S7, for all the metalloporphyrins investigated, the conversion could reach up to above 35.0% with 4-nitrobenzene acid as the main product, and 4-nitrobenzyl Table 1 Oxidation of 4-methyl nitrobenzene in the absence or presence of catalysts



No	Catalysts	Temp. (°C)	Conversion (%)	Selectivity (%	6)		
				R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH
1	_	110	<1	N. D. ^a	N. D	N. D	N. D
2	_	115	<1	N. D	N. D	N. D	N. D
3	_	120	<1	N. D	N. D	N. D	N. D
4	T(4-Cl)PPCo	110	<1	N. D	N. D	N. D	N. D
5	T(4-Cl)PPCo	115	<1	N. D	N. D	N. D	N. D
6	T(4-Cl)PPCo	120	<1	N. D	N. D	N. D	N. D
7	NHPI	110	14.0	18.1	12.9	12.4	56.6
8	NHPI	115	15.7	16.6	14.3	10.1	59.0
9	NHPI	120	16.6	15.8	15.7	7.4	61.1
10	T(4-Cl)PPCo &NHPI	110	29.0	11.8	20.4	6.1	61.7
11	T(4-Cl)PPCo &NHPI	115	30.1	11.1	20.9	5.4	62.6
12	T(4-Cl)PPCo &NHPI	120	31.3	9.9	21.3	4.9	63.9
13 ^b	T(4-Cl)PPCo &NHPI	120	40.4	15.2	25.2	5.1	54.5

Reaction conditions: 4-methyl nitrobenzene (50 mmol, 6.86 g), T(4-Cl)PPCo (0.012%, mol/mol, 0.0049 g), NHPI (5%, mol/mol, 0.41 g), O_2 (1.0 MPa), 8.0 h, 800 rpm

^aNo obvious product detected

^bNHPI (10%, mol/mol, 0.82 g)

alcohol and 4-nitrobenzyl hydroperoxide as the primary byproducts. Especially for the $T(2-OCH_3)PPCo$, the conversion reached up to 49.4% with the selectivity of 64.5% towards 4-nitrobenzene acid, which was a very high level in both of the conversion and selectivity for oxidation of primary benzylic C–H bonds with O₂. More importantly, the protocol in our work was under the solvent-free and additive-free conditions with very low metal catalyst loading, which would facilitate the separation process after reaction and simplify the industrial process for oxidation of primary benzylic C–H bonds. Based on intensive study on the molecular structure of metalloporphyrins investigated herein, the higher activity of $T(2-OCH_3)PPCo$ was mainly ascribed to the ligand $T(2-OCH_3)PP$ decreased the positive charge density around central metal cobalt (II) efficiently as shown in Table S8 obtained from quantum chemical calculation [74]. The fewer positive charges around cobalt (II) would favor the adduction of O_2 to cobalt (II) forming the high-valence metal-oxo complex, followed by the production of phthalimide N-oxyl radical (PINO) and the initiation of the catalytic oxidation cycle [72, 73]. The superior performance of T(2-OCH₃)PPCo in charge transfer was also demonstrated in the electrochemical measurement illustrated in Fig. 3, in which for the typical metalloporphyrins involved, when an external voltage was exerted, the lowest oxidation potential was found for T(2-OCH₃)PPCo. Thus, as a brief summary, the lower positive charge density around central metal cobalt (II) would accelerate the formation of high-valence metal-oxo complex,

 Table 2
 Effect of porphyrin structures on oxidation of primary benzylic C–H bonds catalyzed by metalloporphyrins and NHPI



Entry	Catalysts	Conversion (%)	Selectivity (%))		
			R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH
1	T(2-OCH ₃)PPCo	49.4	10.1	21.5	3.9	64.5
2	T(3-OCH ₃)PPCo	40.7	10.3	24.0	2.6	63.1
3	T(4-OCH ₃)PPCo	38.2	10.9	28.9	2.7	57.5
4	TPPCo	38.3	12.1	22.2	2.6	63.1
5	TPFPPCo	38.6	16.6	16.2	2.6	64.6
6	T(2-Cl)PPCo	43.0	10.5	20.5	2.7	66.3
7	T(3-Cl)PPCo	37.6	12.4	25.0	3.1	59.5
8	T(4-Cl)PPCo	40.4	15.2	25.2	5.1	54.5
9	T(4-COOH)PPCo	43.2	13.4	18.7	2.3	65.6
10	T(2-CN)PPCo	41.5	16.3	18.9	2.4	62.4
11	T(3-CN)PPCo	43.8	15.8	17.3	2.5	64.4
12	T(4-CN)PPCo	40.4	15.2	20.2	2.5	62.1
13	T(2-NO ₂)PPCo	42.3	14.0	17.3	2.7	66.0
14	T(2,6-di Cl)PPCo	40.0	12.2	26.2	2.5	59.1
15	T(2,5-di Cl)PPCo	42.8	11.8	24.9	2.5	60.8

Reaction conditions: 4-methyl nitrobenzene (50 mmol, 6.86 g), metalloporphyrins (0.012%, mol/mol), NHPI (10%, mol/mol, 0.82 g), O_2 (1.0 MPa), 8.0 h, 800 rpm

resulting in the more efficient catalytic oxidation cycles for primary benzylic C–H bonds.

3.4 Effect of Central Metal on Catalytic Oxidation of Primary Benzylic C–H Bonds

With the optimized porphyrin ligand in hands, the effect of central metal on the catalytic oxidation of primary benzylic C–H bonds was investigated systematically, and transition metals such as Co (II), Mn (II), Ni (II), Fe (II), Cu (II) and Zn (II) were selected as metal centers employing 4-methyl nitrobenzene as representative substrate in the presence of 10% NHPI. As illustrated in Tables 3 and S9, for all the porphyrin ligands investigated, the Co (II) complexes exhibited the highest catalytic performance. In the oxidation of 4-methyl nitrobenzene catalyzed by the combination of metalloporphyrins and NHPI, the conversion could reach up to nearly 50% with the selectivity above 60% towards

4-nitrobenzene acid in the presence of Co (II) complexes, meanwhile the conversions were not higher than 30% for other metal complexes without obvious advantage in selectivity too. The superior performance of Co (II) complexes was mainly attributed to their high efficiency in charge transfer and fewer positive charges around central metal Co (II). In the cyclic voltammogram measurement shown in Fig. 4, only the Co (II) complex and Mn (II) complex exhibited obvious oxidation current peaks when an appropriate external voltage was exerted, which meant the existence of charge transfer. For other metal complexes, no apparent current peak was observed, which was consistent with their lower catalytic activity. The discrepancy in the catalytic property between Co (II) and Mn (II) was primarily from the difference in the positive charge density around them (Table S10). The fewer positive charges around cobalt (II) favored the adduction of O_2 to cobalt (II) forming the highvalence metal-oxo complex, followed by the production of Table 3 Effect of central metal on oxidation of primary benzylic C-H bonds catalyzed by metalloporphyrins and NHPI



Entry	Catalysts	Conversion (%)	Selectivity (%))		
			R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH
1	T(2-OCH ₃)PPCo	49.4	10.1	21.5	3.9	64.5
2	T(2-OCH ₃)PPMn	29.8	13.7	12.2	7.7	66.4
3	T(2-OCH ₃)PPNi	18.8	21.6	6.9	17.3	54.2
4	T(2-OCH ₃)PPFe	18.6	16.0	6.3	14.1	63.6
5	T(2-OCH ₃)PPCu	16.4	22.4	14.3	15.3	48.0
6	T(2-OCH ₃)PPZn	17.9	16.9	12.7	23.3	47.1
7	T(2-Cl)PPCo	43.0	10.5	20.5	2.7	66.3
8	T(2-Cl)PPMn	23.0	15.7	14.0	6.8	63.5
9	T(2-Cl)PPNi	15.5	19.9	6.5	16.6	57.0
10	T(2-Cl)PPFe	17.3	17.0	6.0	14.8	62.2
11	T(2-Cl)PPCu	13.8	22.8	7.5	19.8	49.9
12	T(2-Cl)PPZn	17.7	17.3	24.9	16.4	41.4

Reaction conditions: 4-methyl nitrobenzene (50 mmol, 6.86 g), metalloporphyrins (0.012%, mol/mol), NHPI (10%, mol/mol, 0.82 g), O₂ (1.0 MPa), 8.0 h, 800 rpm



Fig. 4 Typical cyclic voltammograms of metalloporphyrins in DMF in scan rate of 100 mV/s

phthalimide N-oxyl radical (PINO) and the initiation of the catalytic oxidation cycle [72, 73]. Thus, due to the delicate cooperation between charge transfer property and fewer

positive charges around cobalt (II), a more efficient catalytic oxidation system for primary benzylic C–H bonds was developed through combining T(2-OCH₃)PPCo and NHPI as binary catalysts under solvent-free and additive-free conditions, in which the metalloporphyrin acted as initiator [72, 73].

3.5 Effect of Catalyst Loading and Pressure

In succession, the effect of catalyst loading and oxygen pressure was explored further with the purpose to realize the catalytic oxidation of primary benzylic C–H bonds more efficiently and under milder conditions, and the 4-methyl nitrobenzene was employed as representative substrate, T(2-OCH₃)PPCo and T(2-Cl)PPCo as catalysts. As illustrated in Tables 4, S11 and S12, with the increase in both of the metalloporphyrins loading and NHPI loading, the conversion of substrate was increased dramatically. For example, the conversion of 4-methyl nitrobenzene was increased from 15.4 to 49.4% as the loading of T(2-OCH₃)PPCo was increased from 0.003 to 0.012% (mol/mol), with the selectivity above 60% towards 4-nitrobenzene acid. To make a Table 4 Effect of metalloporphyrins loading on catalytic oxidation of 4-methyl nitrobenzene



Entry	Metalloporp. loading	Conversion (%)	Selectivity (%)	I		
	(%)		R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH
1 ^a	0.003	15.4	13.3	17.1	8.9	60.7
2 ^a	0.006	24.1	13.2	17.9	6.9	62.0
3 ^a	0.008	30.8	12.4	17.9	6.1	63.6
4 ^a	0.010	35.9	10.3	20.9	4.6	64.2
5 ^a	0.012	49.4	10.1	21.5	3.9	64.5
6 ^b	0.003	16.1	12.8	19.8	4.0	63.4
7 ^b	0.006	28.9	12.2	20.1	3.8	63.9
8 ^b	0.008	32.1	11.9	20.4	3.7	64.0
9 ^b	0.010	36.0	11.6	20.3	3.4	64.7
10 ^b	0.012	43.0	10.5	20.5	2.7	66.3

Reaction conditions: 4-methyl nitrobenzene (50 mmol, 6.86 g), metalloporphyrins (mol/mol), NHPI (10%, mol/mol, 0.82 g), O₂ (1.0 MPa), 120 °C, 8.0 h, 800 rpm

^aT(2-OCH₃)PPCo

^bT(2-Cl)PPCo

balance between catalytic performance and catalyst consumption, the metalloporphyrins loading was set as 0.012% (mol/mol) and the NHPI loading was set as 10% (mol/mol). As for reaction pressure, a similar upward trend like the catalyst loading was observed (Table 5). When the combination of T(2-OCH₃)PPCo and NHPI was utilized as catalyst, the conversion of 4-methyl nitrobenzene increased from to 22.3 to 51.6% with the increase of reaction pressure from 0.40 to 1.20 MPa, and the selectivity towards 4-nitrobenzene acid reached up to 65.7%. Considering the mild conditions and the slight increase in conversion and selectivity, the reaction pressure was suggested not higher than 1.0 MPa. And when air (1.0 MPa) was employed as oxidant, the conversion of 4-methyl nitrobenzene was just 8.2% (Entry 11, Table 5), which could be ascribed to the low concentration of oxidant. Thus, in this work, the oxidant was selected as molecular oxygen (O_2) . Up to now, an efficient and mild protocol in selective oxidation of primary benzylic C–H bonds by O₂ was established employing 4-methyl nitrobenzene as substrate, and the combination of $T(2-OCH_3)PPCo$ and NHPI as catalysts, in which no solvent and no additive was used. The conversion could reach up to nearly 50% with the selectivity above 60% towards aromatic acid, which had a great application potential in the industrial oxidation of primary benzylic C–H bonds.

3.6 Substrate Scope and Comparison with Existing Oxidation Systems

With the efficient protocol for oxidation of 4-methyl nitrobenzene established, the substrate scope was extended from 4-methyl nitrobenzene to a series of typical compounds containing primary benzylic C–H bonds, such as methylbenzene, 1-methylnaphthalene, 4-methyl methylbenzene, 4-chloro methylbenzene and so on. As demonstrated in Table 6, for all the typical substrates, the selective oxidation of primary
 Table 5
 Effect of pressure on catalytic oxidation of 4-methyl nitrobenzene



Entry	Pressure (MPa)	Conversion (%)	Selectivity (%))					
			R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH			
1 ^a	0.40	22.3	19.1	10.3	9.3	61.3			
2 ^a	0.60	25.2	17.3	13.9	6.2	62.6			
3 ^a	0.80	37.7	14.6	17.6	4.9	62.9			
4 ^a	1.00	49.4	10.1	21.5	3.9	64.5			
5 ^a	1.20	51.6	9.4	21.6	3.3	65.7			
6 ^b	0.40	23.0	14.6	15.0	8.4	62.0			
7 ^b	0.60	25.9	11.0	16.9	7.9	64.2			
8 ^b	0.80	37.9	10.9	18.4	5.9	64.8			
9 ^b	1.00	43.0	10.5	20.5	2.7	66.3			
10 ^b	1.20	44.8	10.7	20.7	2.2	66.4			
11 ^c	1.00	8.2	15.8	18.1	12.7	53.4			

Reaction conditions: 4-methyl nitrobenzene (50 mmol, 6.86 g), metalloporphyrins (0.012%, mol/mol, 0.0049 g), NHPI (10%, mol/mol, 0.82 g), O₂, 120 °C, 8.0 h, 800 rpm

^aT(2-OCH₃)PPCo

^bT(2-Cl)PPCo

^cT(2-OCH₃)PPCo (0.012%, mol/mol), NHPI (10%, mol/mol), air (1.0 MPa)

benzylic C–H bonds could be accomplished under mild conditions with aromatic acids as the primary products, especially for methylbenzene, 4-phenyl methylbenzene, 4-chloro methylbenzene, 4-fluoro methylbenzene and 2,4-dichloro methylbenzene, for which the selectivity towards aromatic acids reached up to 92.3%, 91.6%, 95.1%, 94.6% and 94.1% respectively with the acceptable conversions (35.1%, 73.5%, 88.5%, 85.3% and 63.2%). For other typical substrates, the selectivity towards aromatic acids also reached up to higher than 60%, and the primary products were 1,4-dicarboxybenzene and 1,3-dicarboxybenzene for 4-methyl methylbenzene and 3-methyl methylbenzene as substrates. Based on the satisfying substrate tolerance, the method disclosed in this work could be regarded as an efficient strategy in selective oxidation of primary benzylic C–H bonds with O₂ employing the combination of T(2-OCH₃)PPCo and NHPI as catalysts under the solvent-free and additive-free conditions. Then the strategy in this work was compared with some reported methods in oxidation of primary benzylic C–H bonds with O₂, which had been demonstrated in Table 7 clearly that the major superiorities of our route were no solvent, no additive, mild conditions, and higher selectivity towards aromatic acids, which made the route for primary benzylic C–H bonds oxidation more simple and practical, and more suitable for industrial application. This work also was a significant example in which the effect of the metalloporphyrins structures on selective oxidation of C–H bonds was explored systematically. In addition to the satisfying substrate tolerance, an enormous function was endowed to the current route as an important reference for other C–H bonds
 Table 6
 Oxidation of primary benzylic C–H bonds catalyzed by metalloporphyrins and NHPI



Entry	Substrates	Conversion (%)	Selectivity (%	5)		
			R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH
1	CH ₃	35.1	3.7	N.D. ^a	4.0	92.3
2	CH ₃	30.4	14.8	N.D	6.3	78.9
3	CH ₃	35.4	13.4	N.D	5.3	81.3
4 ^b	CH ₃	73.5	1.8	N.D	6.6	91.6
5°	H ₂ C CH ₃	27.3	9.6	N.D	N.D	81.3
6 ^d	H ₃ C CH ₃	14.8	14.9	N.D	N.D	71.4
7	H ₃ CO	34.2	18.3	4.2	5.7	71.8
8 ^e	CI CH ₃	8.4	20.1	N.D	23.1	56.8
9	CI CH ₃	11.3	14.4	N.D	20.2	65.4
10	CI CH3	88.5	1.0	1.6	2.3	95.1
11	F CH ₃	85.3	1.2	2.4	1.8	94.6

Table 6 (continued)EntrySubstratesConversion (%)Selectivity (%) R_1 -OOH R_1 -OH R_2 -CHO R_2 -COOH12 $\downarrow \downarrow $						
Entry	Substrates	Conversion (%)	Selectivity (%	(j)		
			R ₁ -OOH	R ₁ -OH	R ₂ -CHO	R ₂ -COOH
12	CI CH ₃	63.2	2.1	N.D	3.8	94.1
13	O ₂ N CH ₃	49.4	10.1	21.5	3.9	64.5

Reaction conditions: substrate (50 mmol), T(2-OCH₃)PPCo (0.012%, mol/mol, 0.0048 g), NHPI (10%, mol/mol, 0.82 g), O₂ (1.0 MPa), 8.0 h, 120 °C, 800 rpm

^aNo obvious product detected

^b100 °C

^c1,4-dicarboxybenzene as main product

^d1,3-dicarboxybenzene as main product

^eT(2-Cl)PPCo (0.012%, mol/mol, 0.0049 g)

oxidative functionalization using the clean O_2 as oxidant under mild conditions.

4 Conclusions

The efficient and selective oxidation of primary benzylic C-H bonds by O₂ under solvent-free and additive-free conditions was achieved employing the combination of metalloporphyrins and NHPI as binary catalysts. Based on the systematical investigation on the effects of reaction temperature, porphyrin structure, central metal, catalyst loading and O₂ pressure, the optimized catalytic system was obtained as the combination of T(2-OCH₃)PPCo and NHPI, in which all the typical substrates possessing primary benzylic C-H bonds could be catalytically transformed to their oxygen-containing products at 120 °C and 1.0 MPa O₂ with aromatic acids as the primary products. For the typical substrates such as methylbenzene, 4-phenyl methylbenzene, 4-chloro methylbenzene, 4-fluoro methylbenzene and 2,4-dichloro methylbenzene, the selectivity towards aromatic acids reached up to 92.3%, 91.6%, 95.1%, 94.6% and 94.1%

with the conversions of 35.1%, 73.5%, 88.5%, 85.3% and 63.2% respectively. The superior performance of T(2-OCH₃) PPCo among the metalloporphyrins involved was mainly attributed to its high efficiency in charge transfer and fewer positive charges around central metal Co (II) which favored the adduction of O_2 to cobalt (II) forming the high-valence metal-oxo complex, followed by the production of phthalimide N-oxyl radical (PINO) and the initiation of the catalytic oxidation cycle. Compared with the existing primary benzylic C-H bonds oxidation systems, the main superiorities of the route in this work were no solvent, no additive, mild conditions, higher selectivity towards aromatic acids and satisfying substrate tolerance. To the best of our knowledge, this work is a very scarce and significant instance in the oxidative functionalization of primary benzylic C-H bonds without any solvent or additive used under milder conditions, which not only provided an efficient and practical protocol in utilization of widely available and inexpensive hydrocarbons containing primary benzylic C-H bonds, but also would present a significant reference in both academic research and industrial application for the construction of more efficient C-H bonds oxidation systems.

Entry	Main products	Conditions	Conversion (%)	Selectivity (%)	Refs.
1	СООН	T(4-Cl)PPMnCl, NHPI, CTAB, O ₂ , 100 °C	41.0	70.6	[52]
2	СООН	CoOx/SiO ₂ , NHPI, AcOH, O ₂ , room temperature	75.2	93.5	[14]
3	СООН	Cobalt in N-doped carbon nanotube, O_2 , 120 °C	23.2	60.9	[75]
4	СООН	Co(OAc) ₂ , NHPI, ionic liquid, O ₂ , 100 °C	80.0	78.0	[41]
5	СООН	Immobilized phthalocyanine iron, NHPI, O ₂ , CH ₃ CN, 80 °C	35.3	71.8	[53]
6	СООН	Co-SBA-15@ NDHPI, O ₂ , CH ₃ CN, 90 °C	29.9	89.3	[32]
7	СООН	Immobilized NDHPI, O ₂ , CH ₃ CN, 90 °C	18.6	60.7	[33]
8	СООН	Au nanoparticles, NHPI, O ₂ , CH ₃ CN, 60 °C	60.1	99.6	[37]
9	НаСО СООН	TPPMnCl, O ₂ , Cyclohexene, CH ₃ CN, 160 °C	14.0	44.3	[44]
10	СООН	Immobilized NHPI, Co(OAc) ₂ , AIBN, AcOH, O ₂ , 80 °C	17.7	24.0	[34]
11	СНО	Immobilized NHPI, Co(OAc) ₂ , AIBN, AcOH, O ₂ , 80 °C	17.7	44.0	[34]
12	Н3СО СООН	Co(OAc) ₂ , NHSI, Mn(OAc) ₂ , O ₂ , CH ₃ CN, 150 °C	99.5	99.6	[18]
13		Co(OAc) ₂ , NHSI, CH ₃ CN, O ₂ , 40 °C	>99.0%	96.0	[40]
14	$H_{3}C^{SI} O^{SI} CH_{3}$ $CH_{3} CH_{3}$ CHO	CoOx/SiO ₂ , NHPI, HFIP, O ₂ , room temperature	92.2	69.7	[14]

Table 7 Comparison with some existing primary benzylic C-H bonds oxidation systems employing O2 as oxidant

Table 7 (continued)

Entry	Main products	Conditions	Conversion (%)	Selectivity (%)	Refs.
15	СНО	Copper particles in graphene, O ₂ , acetone, 110 °C	9.0	98.0	[39]
16	СНО	Co(OAc) ₂ , NHPI, HFIP, O ₂ , room temperature	62.0	99.0	[38]
17	СНО	Anion modified mesoporous oxides, O_2 , 120 °C	5.1	48.0	[15]
18	СНО	Immobilized phthalocyanine iron, NHPI, O ₂ , CH ₃ CN, 80 °C	23.7	56.4	[53]
19	CHO	TPPMnCl, O ₂ , Cyclohexene, CH ₃ CN, 160 oC	7.2	66.7	[44]
20	СООН	T(2-OCH ₃)PPCo, NHPI, O ₂ , 120 °C	35.1	92.3	This work
21	СООН	T(2-OCH ₃)PPCo, NHPI, O ₂ , 120 °C	88.5	95.1	This work
22	СООН	T(2-OCH ₃)PPCo, NHPI, O ₂ , 120 °C	73.5	91.6	This work

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